Sol-gel preparation of pure and doped TiO_2 films for the photocatalytic oxidation of ethanol in air

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Abstract

Stable sols of TiO_2 were synthesized by a non-aqueous sol-gel process using titanium (IV) isopropoxide (TTIP) as precursor. The microstructure, optical and morphological properties of the films obtained by spin-coating from the sol, and annealed at different temperatures, were investigated using SEM, TEM, diffuse reflectance spectroscopy (DRS) and ellipsometry. The crystalline structure of the films was characterized by X-ray diffraction and their photocatalytic activity was evaluated for the oxidation of ethanol in air. The influence of the calcination temperature, pre-heat treatment and the number of layers was studied. Simultaneous thermo-gravimetric and differential thermal analysis (TG/DTA) measurements were carried out to ascertain the thermal decomposition behavior of the precursors.

In order to obtain a higher photoresponse in the visible region, a series of vanadium-, niobium- and tantalum-doped TiO_2 catalysts was synthesized by the same sol-gel method. For V doping two different precursors, a vanadium alkoxide and V_2O_5, were used. The effect on the crystallization and photocatalytic activity of the doped TiO_2 films was investigated. Furthermore, to identify the effective composition of the samples, they were characterized by X-ray photoelectron spectroscopy (XPS) and the surface area of the powders was measured by N_2 adsorption. The 10wt.% doped catalysts exhibit high photocatalytic activity under visible light and among them the best performance was obtained for the sample containing Ta as dopant. The crystallite sizes are closely related to the photocatalytic activity.

Keywords: *TiO_2 photocatalyst; doping effect; visible photocatalytic activity*.

1 Introduction

Global warming and emission of hazardous pollutants into air and water are serious environmental problems that need to be addressed. In recent years, public and legislators' awareness of the importance of a clean environment has increased and this has prompted the research activity into the development of technology for pollutant abatement. For this purpose, photocatalysis, allowing the complete breakdown of a wide spectrum of polluting substances using air oxygen as oxidant and operating at room temperature and atmospheric pressure, is

becoming increasingly attractive. In particular, effective removal of highly hazardous pollutants such as volatile organic compounds (VOCs) from contaminated indoor atmospheres, can be successfully accomplished by applying photocatalysis. VOCs indeed have been recognized as one of the most important groups of air contaminants since their emission has many environmental implications, among which the increase in the formation of photochemical smog and the depletion of the atmospheric ozone layer [1]. In recent years, titanium dioxide, widely used because of its many applications in optical and technological fields [2,3], stood out among the various semiconductor materials, for its photocatalytic properties for air and water-purification [4-6].

For the preparation of TiO_2-based photocatalyst thin films, many methods are available, such as solvothermal synthesis [7,8], electron beam evaporation [9], chemical vapor deposition [10] and sputtering [5,11-13]. The sol-gel technique [2,14,15] equally proved to be an efficient and versatile method to prepare TiO_2 fine powders and films, allowing to control the stoichiometry and achieve high purity and homogeneity of the final product. It allows to work in mild and ambient atmospheric conditions and obtain highly porous and nanocrystalline materials. Since pure TiO_2 only absorbs light with wavelengths shorter than 380nm (UV region), it is necessary to increase its spectral sensitivity to visible light for more practical applications [2,16,17]. In this work, the sol-gel method was employed to prepare vanadium-, niobium- and tantalum-doped TiO_2 catalysts in order to increase visible light efficiency. For V doping, a vanadium alkoxide and V_2O_5 were used to obtain a different distribution of the vanadium ions in the TiO_2.

2 Experimental

2.1 Materials. All chemicals for the TiO_2 sols preparation were used as received from Alfa Aesar: titanium (IV) isopropoxide (TTIP; ≥ 97%), acetylacetone (AcAc; 99%), ethanol (EtOH; HPLC grade), acetic acid glacial (99%), vanadium (IV) triisopropoxide oxide ($VO[CHO(CH_3)_2]_3$; 96%), vanadium (V) oxide (V_2O_5; 99.8%), niobium ethoxide (NbE; 99.9%), tantalum ethoxide (TaE; optical grade, 99.95%) and hydrogen peroxide (H_2O_2, 35% w/w aq. Soln.). The TiO_2 (Degussa P25) reference photocatalyst was obtained from Degussa Chemical, Germany.

2.2 Catalyst preparation. Precursor sols for TiO_2 were prepared as follows: TTIP was dissolved in ethanol and then acetylacetone was added under magnetic stirring at room temperature in order to decrease the reactivity of the alkoxide and stabilize the sol [14,18]. After 1 hour, a mixed solution of acetic acid and ethanol was added drop wise under stirring to initialize the hydrolysis by esterification reaction with alcohol. The molar ratio TTIP:EtOH was maintained at 1:10, whereas the molar ratio TTIP: AcAc: acetic acid was kept at 1: 0.3: 0.2 [18]. The obtained mixture was stirred for 1 hour, resulting in a TiO_2 sol, which was stable for more than 5 months.

Doped TiO_2 sols were prepared by dissolving titanium isopropoxide and the dopant alkoxide in ethanol and then following the same procedure as described above. Appropriate volumes of V, Nb and Ta alkoxides [19,20] were added to the reaction with TTIP and EtOH to obtain dopant precursor amounts of 10 and 20 wt.%. The synthesis of V doped TiO_2 with vanadium oxide as precursor involved the dissolution of V_2O_5 in H_2O_2 [21]. The molar ratio V_2O_5 : H_2O_2 was kept at 1:1.3 [22] and the resulting solution was stirred for 30 minutes. Afterward it was added to a mixture of TTIP, EtOH and AcAc and the same procedure as described above was followed to obtain the sol.

Sodium free glass slides of 5 cm x 5 cm x 0.7mm (Corning 1737F) were used as substrates for spin coating in order to prevent the inhibition of the photocatalytic activity by sodium uptake from the substrate [23]. Before

coating, the substrate was cleaned with a N_2 flux. The sols were deposited onto the substrates and spun at 2000 rpm with a photoresist spinner (Headway Research Inc. USA) for 20 sec. After coating, the films were dried at 100°C for 8 h and calcined at 400, 500 or 550°C for 2h in air. Some samples were not heated at 100°C to evaluate the pre-heat treatment influence. In addition, samples with a different number of layers were prepared. In between coatings, the glass slides were placed in an oven at 80°C, to achieve complete evaporation of the solvent after every coating.

As a reference sample, a suspension of TiO_2 Degussa P25 was prepared by dissolution of 0.1g powder in 5ml of isopropanol. It was kept under magnetic stirring for 1 h at 300 rpm and then sonicated for 10 minutes. The reference film was prepared by spin coating the P25 suspension at 2000 rpm for 20 sec. This coating was repeated four times and between subsequent coverings the glass slides were heated to 80°C to remove the solvent [24].

2.3 ***Characterizing measurements.*** The crystalline structure of the thin films was analyzed by XRD (Siemens Kristalloflex DS5000) using CuKα radiation in the range of 20-60° (2θ). The film thickness was determined, for the most homogeneous films, using spectroscopic ellipsometry (SE, J.A. Woollam Co. Inc., M-2000FI). The fitting over the region of 250-1700nm was performed using the Complete Ease Software (Woollam Inc.) using the B-spline parametrization for the refractive index dispersion. Scanning electron microscope (SEM, FEI Quanta 200F) was used, in low vacuum mode, to examine the surface morphology of the films.

Diffuse reflectance measurements, used to measure the band gap width, were performed on a Varian Cary 500 UV/Vis/NIR spectrophotometer, equipped with an integrating sphere, using $BaSO_4$ as reference. Samples were prepared by packing the powder between C tape and a quartz glass. UV/Vis spectra were recorded in the range of 250-800 nm in diffuse reflectance mode and converted to the absorbance coefficient *F(R)* by the Kubelka-Munk equation [25].

Thermogravimetric and differential thermal analyses (TGA/DTA) were carried out, using a SDT 2960-TA instrument (heating rate: 5°C/min from room temperature to 600°C in flowing air), to study the thermal decomposition of the sols.

Nitrogen adsorption-desorption isotherms were measured at 77 K on a Fisons Sorptomatic 1990 after outgassing the powders for 24 h at room temperature. Textural properties were calculated using a coherent set of well-known techniques [26].

Film composition and the oxidation state of the doping elements were determined by X-ray photoelectron spectroscopy (XPS), using a S-Probe monochromatized XPS spectrometer (VG) equipped with an Al Kα X-ray source (1486.6 eV). In order to eliminate the outer contaminant layers of the samples, argon sputtering (pressure 1.5×10^{-7} mbar) with an energy of 4keV was performed during 40s. The Ti2p, V2p, O1s, Ta4f and Nb3d lines were recorded and their binding energies were referenced to the 1s photoline of carbon originating from contaminant hydrocarbons (284.6 eV).

Transmission electron microscopy (TEM) analysis of the doped catalysts was performed with a 200keV Cs-corrected microscope (JEOL FE2200). For TEM studies, the sample was scratched off the substrate and then dispersed in ethanol. Then they were dropped and dried on carbon-coated copper grids.

2.4 Photocatalytic measurements. Photocatalytic measurements were carried out in a stainless steel batch reactor, in a controlled Ar/O_2 atmosphere (ratio 80:20 to simulate air). The reaction chamber was first evacuated and then back-filled with the Ar/O_2 atmosphere at 1.05×10^5 Pa. Ethanol (absolute PA, Panreac, Spain) was

injected in the chamber in a concentration of 273 ppm and monitored by means of an atmospheric gas analyzer containing a mass spectrometer (MS, Pfeiffer Vacuum Omnistar). A mercury high-pressure short arc bulb (Osram HBO 200W/2) was used as light source with an input power of 100 W. The thin films were positioned 15 cm from the lamp and their temperature was maintained at 40°C during the measurements. For measurements limited to visible light, a poly-methyl methacrylate (PMMA) filter was used to cut off the UV light. The concentration of ethanol was monitored in time using the MS peak at 45 amu and the initial reaction rate was determined from the slope of the first linear data points measured during the breakdown reaction into CO_2 and water.

3 Results and discussion

The influence of pre-heat treatment, calcination temperature and different number of layers on the photocatalytic activity of the undoped films was tested in order to choose the best film preparation conditions. Table 1 shows a list of all the titania photocatalysts prepared, together with the number of layers, the conditions adopted for the preparation, the photocatalytic activity of the films and their thickness. In the penultimate column the average crystallite sizes, calculated using the Scherrer equation [27] are reported. Most films displayed only diffraction peaks from anatase and the width of the most intense diffraction peak (101), corrected for the instrumental broadening, was used for crystallite size determination.

The effect of pre-heat treatment at 100°C can be derived from samples A and D in Table 1. The photocatalytic performance of the pre-heat treated film A is twice as good as sample D which was not pre-heat treated. The film structure is not affected by pre-heat treatment (not shown), but the larger crystallite size in sample D leads to a lower photocatalytic activity than for the pre-heated sample A. Indeed, the increase in the crystallite size, by decreasing the effective surface area, induces a lower activity.

From the data obtained in the photocatalytic tests, it is possible to observe that a mild increase in the photocatalytic activity was achieved by adding a second coating (sample A and B). Several authors reported that this increase causes an enhancement of the photocatalytic activity until it reaches a maximum value, after which the activity remains constant [28, 29]. For three deposited coatings (sample C), there is a decrease in the activity. It can be seen from the XRD pattern (Fig. 1) that the structure of the TiO_2 single and double layer is mainly of anatase phase type, whereas the sample with 3 coatings consists of anatase and rutile peaks. The lower photocatalytic activity of the triple layer film (sample C) can thus be ascribed to the presence of rutile, which is less reactive than anatase because of its higher recombination rate of photoinduced electrons and holes [30] and to the increased crystallite size (Table 1).

The effect of the calcination temperature was also investigated (samples B, E and F). The XRD patterns evidence peaks belonging to pure anatase and no trace of rutile is detected in any sample, treated at 450, 500 and 550°C. Hence, the anatase phase remains stable in thin films up to 550°C. However, an increase in the annealing temperature results in crystallite growth and therefore in worse photocatalytic performance. In addition, it was found that the thickness of the film baked at 550°C is higher than the thickness of the films calcined at lower temperatures and this can be ascribed to the growth of the inter grain porosity as a consequence of the increase of the particle size by coalescence [18].

From the above-mentioned results, best conditions for the preparation of the films were selected: pre-heat treatment at 100°C, double coating and calcination at 450°C. Indeed, the activity of sample B comes close to the

one of the reference photocatalyst P25. In order to understand the evolution of phases and prove the complete decomposition of the precursors upon thermal treatment, the gel was subjected to thermogravimetric and differential thermal analysis.

Figure 2 shows TGA and DTA on TiO_2 gel. The weight loss occurred in three temperature regions and above 530°C the weight loss curve leveled off. The first loss appears between 150 and 230°C and is attributed to the loss of physically absorbed water from the precursor. No peaks in the DTA curve are observable in this region, therefore this loss cannot be ascribed to the evaporation of the solvent or to the thermal decomposition occurring during gelation. The second weight loss between 250 and 350°C is related to a weak extended exothermic peak in the DTA plot. It is considered to originate from the calcination of organic compounds and from dehydroxilation processes. The third weight loss step centered at 515°C corresponds to the removal of hydration water and OH surface groups as well as to the further combustion of the remaining organic compounds [31]. All exothermic peaks in the DTA plot are related to weight loss, indicating that no phase transformation has occurred and this is in agreement with the XRD results.

To shift the absorption edge towards the visible region and increase the photocatalytic activity under visible light, elements of the fifth group were doped into the TiO_2 sols at two concentrations (10 and 20 wt.%). Table 2 summarizes the loading of dopants, the results of the photocatalytic tests, the crystallite sizes and the lattice parameters of the doped catalysts, all doubly coated films pre-heated at 100°C and calcined at 450°C. The photocatalytic activities of the films, obtained under visible and ultraviolet + visible light irradiation, are also reported in Table 2 and compared with a pure TiO_2 sample (sample B). As expected, the latter was not active under visible light.

The presence of dopants remarkably influences the morphology of the films. Indeed, all samples present a unique texture that is not always crack free or homogeneous (Fig.3a-e). From XRD analysis (not shown) all doped samples showed only peaks belonging to the anatase phase. Slight shifts in peak position were observed, indicating lattice distortion in the anatase crystal structure (Fig.4). The absence of peaks of dopant phase, points out that the dopant species are either well dispersed in the TiO_2 phase or amorphous.

TEM was used to further investigate the morphology and the particle size of the samples. The examined area of doped TiO_2 catalysts show that the particle sizes are consistent with XRD results. Fig. 5 (a, b and c) displays the TEM micrographs of V3, Ta2 and Nb1, respectively, and it can be seen that the particle sizes of V3 are around 20nm, those of Ta2 range from 60 to 100 nm, while for Nb1 the particles size is bigger (~100nm). In addition, it can be estimated that the particles in V3 and Ta2 present mostly spherical morphology.

In Table 2, the specific surface areas obtained by Brunauer, Emmett and Teller (BET) method, S_{BET}, are presented for the undoped titania and all the doped TiO_2 powders. For V3 and V4 samples, it might be expected a larger surface area due to the very small crystallite size. However, the presence of some impurities, such as solvent or reactants, into the pores of the samples could have reduced the sample surface area measured by BET. Upon V1 and V2, S_{BET} is higher than what could be expected taking into account the crystallite diameters calculated by XRD. Indeed, nitrogen adsorption-desorption isotherms of these samples (not shown) are characteristic of slightly microporous samples. Furthermore, the difference between BET and XRD data for V1 and V2 might be due to the fact that the samples particles can have different shape (not only spherical as shown in TEM images). So all these phenomena - pores and roughness - should be taken into account. The specific

surface areas for Ta and Nb doped TiO_2 are in quite good agreement with the XRD crystallite average diameters and it can be pointed out that Nb dopants act as growth promoter, increasing the particle size.

The band gap (Fig.6) of Nb and Ta doped TiO_2, compared to non-doped TiO_2 (sample B), showed an absorption edge (Table 2) shifted to higher energy and this is due to band filling effects (Moss-Burstein shift) [32,33]. Upon V doping the samples synthesized from alkoxide showed a red-shift whereas the ones from V_2O_5 presented a blue-shift. This is consistent with the quantum confinement model (QC)[34]. According to QC theory, for semiconductor particles below 30 nm, both electrons (in the conduction band) and holes (in the valence band) are spatially confined by the surface potential barrier. This confinement results in an increase in energy of the lowest energy optical transition from the valence to the conduction band, that is an increase of the band gap.

To determine the actual composition and chemical states of dopants in the samples, XPS spectra (Fig. 7a-c) were recorded. V-doping TiO_2 catalysts existed in one of 3 chemical states, which are V^{5+} at 517.3 eV (sample V3), V^{4+} at 515.9eV (sample V1 and V4) [35] and a vanadium species that is a mixed-valence oxide consisting of V^{4+} and V^{5+} at 516.3eV (sample V2)(Fig.7a). Hence, XPS analysis showed that V species exist in different oxidation states in the lattice of V-TiO_2 although in both syntheses V^{5+} was used as precursor for the vanadium ions. Taking into account the reduction potentials it can be assumed that the reduction of V^{5+}-V^{4+} was accompanied by the oxidation of the alcohol used in the synthesis [36]. However, V reduction can also be due to the 40s Ar^+ bombardment, before the actual the XPS measurement. Indeed, it is well known that the ion sputtering performed in XPS measurements induces considerable modification in the surface composition and in the morphology of a sample. In particular, it is reported that by argon bombardment different vanadium oxidation states can be obtained from V_2O_5 and that the first reduction from V^{5+} to V^{4+} occurs after only 12 sec of sputtering [37]. However, additional study will be required in order to understand the reason why in V3 only V^{5+} ions were detected by XPS.

The peaks of the Nb3d were very weak and not well resolved (Fig. 7b). The binding energies for the 20wt.% Nb doped catalyst were found to be at 207 and 210 eV, suggesting that the oxidation state of Nb in both Nb-doped samples is 5+ [38]. The XPS spectra of the Ta-4f level showed a very weak and broad peak (Fig.7c). In particular, for the sample Ta1 this peak appeared clearly as two shoulders, at about 27 and 22 eV. These binding energies are nearly the same as those reported for Ta_2O_5 and Ta metal, respectively [38].

In terms of the Ti2p XPS spectra (not shown), the spin orbit components ($2p_{1/2}$ and $2p_{3/2}$), corresponding to Ti^{4+} in a tetragonal structure, are well represented by two narrow peaks at about 464.0 and 458.5 eV [39]. A further confirmation of this assumption is given by the fact that the difference in BE between the spin orbit components of the Ti2p peak is about 5.6eV, that is proper to Ti^{4+} and excludes the presence of other oxidation states for all the doped samples [40].

The O1s XPS (not shown) spectra showed a broad and slightly asymmetrical peak indicating that there was more than one chemical state according to the binding energy. In particular, deconvolution of the O1s spectra yielded peaks consistent with O^{2-} (~529.5eV), OH^- (~530.5eV) and adsorbed H_2O (~532eV), respectively [41-45].

Table 3 lists the nominal and real surface element/Ti ratios as well as the binding energies for all elements recorded in XPS and referenced to C1s at 284.6 eV.

A quantitative analysis of the composition showed hardly any deviation of the relative atomic concentration of elements in for Nb- and Ta-doped TiO_2. For V-doped samples, the actual surface doping concentration is quite

low, especially for the samples containing a dopant/Ti ratio of 10wt.%. The XPS measurements indicated that the concentration of vanadium in TiO_2 matrix is much lower than the nominal values for 10 wt.% vanadium doped films synthesized from both precursors. Since the presence of dopants was confirmed from other sample properties, like color (brownish and greenish for V1, V2 and V3, V4, respectively), and slight variation of the lattice parameters, the low actual concentration determined by XPS can be ascribed to an appreciable loss of dopant occurring during the removal of the upper surface layer. This was confirmed by XPS depth profiling, performed on the V-doped TiO_2 samples (Fig. 8). After the first sputtering, which entails the removal of about 4nm of sample, the presence of a V peak is clear (dotted line). However, after a second sputtering no trace of dopant is evident from XPS spectra. This may indicate that the sol-gel technique does not allow the addition of V ions equally distributed in the bulk of the sample but they are only concentrated on the surface, and in particular in the upper 8nm of sample, taking into account that during the 40s Ar^+ bombardment a thickness approximately equal to 4nm is removed. On the other hand, the different distribution of the dopant ions can also be due to the calcination which may have induced a surface enrichment [46].

Regarding to photocatalysis, under UV+visible illumination, the doped samples clearly perform far worse than the undoped sample B. However, with the UV filter in place, the visible activity of the undoped sample is reduced to almost zero, while the doped samples now prove more active: compared to undoped sample B, all samples except Ta2 and Nb2 perform better under visible illumination.

For V3 and V4, the improvement in the photocatalytic activity under visible irradiation might be due to highly dispersed vanadium in the TiO_2 crystallites [47]. Indeed, the lattice parameters determined from the XRD pattern, indicated that a distortion occurred in the pure anatase structure (sample B). In particular a decrease of lattice parameters a and c was observed due to the presence of V^{5+} (59pm) or V^{4+} (69pm) ions inserted in the lattice for all V doped samples, except for the 20wt.% V sample synthesized from alkoxide which shows larger lattice parameters although the ionic radii of the ions present in the sample are smaller or similar to Ti^{4+} (Table 2). Under visible illumination, both the 10wt.% and 20wt.% V synthesized from V_2O_5 are better that the corresponding ones derived from alkoxide. This can be ascribed to the smaller crystallite size and hence the higher surface area of the film.

The visible response of Ta1 was the largest of all doped TiO_2 films. It can be ascribed on the other hand to a similar ionic radius for both titanium and tantalum ions, which is about 68pm as well as to the smaller crystallite size. For the 20wt.% Ta doping, however, the visible response has dropped to zero. Following the characterization properties of Table 2, this must be ascribed to the higher doping concentration giving rise to larger crystallite sizes. Although Nb has a similar ionic radius (69pm) as Ta, the lower activity of Nb-doped samples can be explained taking into account an enhanced electron–hole pair recombination rate due to the modification in the anatase lattice induced by doping and cation vacancy formation [48-50].

In conclusion, doping the TiO_2 films with elements having a similar ionic radius favors easy inclusion of these elements into the lattice, with slight lattice distortions of the titania host. The crystallite size stood out to be a most important parameter in determining the visible photoresponse. Hence, preparation should aim at further decreasing the crystallite size of doped titania.

The 10wt.% Nb and V doped titania samples showed a higher activity under visible light than under UV + visible irradiation. This is a highly surprising and unexpected result. However, careful analysis showed that this

is indeed an existing and reproducible effect, and no artifact of the measurements. As the temperature of the sample is kept constant (at 40°C) during the photocatalytic measurement, a thermal effect is probably not responsible for the observed phenomenon. The effect might be ascribed to a slower recombination of photoinduced hole/electron pairs. In particular, since the charge transfer competes with the hole-electron recombination process, it can be hypothesized that, due to the doping, the higher is the energy of the light reaching the sample, the higher is the probability of recombination. Therefore, the higher energy of the UV light might lead to a faster recombination of electron-hole pairs which results in a lower photocatalytic activity. Further analysis is in progress to clarify the mechanism which led to a higher visible response. The result, however, stresses the importance of using the same light source for UV/visible and visible photocatalysis. Usually, completely different light sources are applied for the two experiments, and absolute activities cannot be compared directly.

4 Conclusions

In the present work, the photocatalytic activity of TiO_2 catalysts films prepared by the sol-gel method was studied as a function of the pre-heat treatment, calcination temperature and number of coatings. The photocatalytic activity of the most active film (doubly coated, pre-heat treated at 100°C and calcined at 450°C) was found to be comparable to a reference sample of Degussa P25. The thickness and crystallite size control of the TiO_2 films were found to be very important to obtain good photocatalytic activity.

The modification of TiO_2 catalyst to sensitize it to visible light, by addition of dopants, was also studied. 10 and 20 wt.% V-, Nb and Ta-doped titania catalyst films were synthesized. The doping process was successful and the dopant atoms were inserted into the TiO_2 lattice as confirmed by XRD and XPS analysis. All doped samples have higher activity than pure TiO_2 under visible light irradiation. Our studies show that V-TiO_2 catalysts prepared using V_2O_5 as precursor, perform better under visible irradiation than V samples synthesized from alkoxide and this can be ascribed to the smaller crystallite sizes. Among the developed catalysts, the 10wt.% doped TiO_2 samples are the most active films and in particular the10wt.% Ta doped titania shows the highest photocatalytic activity in the visible region, which is attributed to a similar ionic radius and small crystallite sizes.

For some of the 10wt% samples, the photocatalytic activity under visible illumination is higher than the activity under UV+visible illumination. It shows that photocatalytic experiments using different wavelength ranges should – unlike usual practice – be carried out with the same light source and only using filters. In this way, a direct comparison of activities at these different wavelengths is possible.

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Figure Captions

Fig. 1 XRD spectrum of TiO_2 films with different number of layers. Diffraction peaks A: anatase (ICDD card no. 21-1272) and R: rutile (ICDD card no. 21-1276).

Fig. 2 TGA (solid line) and DTA (dashed line) profiles of TiO_2 gel.

Fig. 3 SEM images of the surface morphology of undoped **(a)** and doped TiO_2 thin films: V4 **(b)**, V2 **(c)** Nb2 **(d)** and Ta2 **(e)**.

Fig. 4 Enlargement of the region around 25° 2θ of pure and doped TiO_2 powders heat treated at 450°C.

Fig. 5 TEM micrograph of V3**(a)**, Ta2 **(b)** and Nb1**(c)**

Fig. 6 Diffuse reflectance spectra of sol-gel made samples listed in Table 2.

Fig. 7 The XPS spectra of dopant photolines **(a)** V2p, **(b)** Nb3d and **(c)** Ta4f.

Fig. 8 The XPS depth profile spectra of sample V4.

Table 1. Properties of the undoped synthesized photocatalysts

Sample	Number of layers	Pre heat treatment 100° C	Calcination temperature (° C)	Photocatalytic activity ± 3σ [a] (ppm/min)	d(nm)**	Thickness [b] (nm)
A	1	Yes	450	3.09 ± 0.23	74	40
B	2	Yes	450	3.24 ± 0.28	68	190
C	3	Yes	450	1.76 ± 0.15	84	310
D	1	No	450	1.87 ± 0.30	109	270
E	2	Yes	500	0.60 ± 0.05	77	215
F	2	Yes	550	0.49 ± 0.06	95	340
P25	4	—	—	3.44 ± 0.16	25	n.a.

[a] The results are reported with 99.7% confidence interval.

[b] The thickness was determined by means of ellipsometry measurements performed on the most homogeneous films. (n.a.: not applicable)

** Crystallite sizes d are calculated from XRD peak widths

Table 2. Properties of V, Nb and Ta- doped samples

Sample	Dopant content (wt.%)	Photocatalytic activity UV+visible ± 3σ [a] (ppm/min)	Photocatalytic activity visible ± 3σ [a] (ppm/min)	d(nm)**	Lattice parameters [b] a(Å)	c(Å)	Band gap energy† (eV)	S_{BET} ± 5 (m^2/g)
B	—	3.24±0.28	0.02±0.01	75	3.7903	9.7141	2.72	35
V1	10	0.05±0.02	0.16±0.09	61	3.7868	9.5919	2.25	55
V2	20	0.07±0.01	0.09±0.03	78	3.7937	9.8251	2.90	60
V3	10	0.076±0.004	0.23±0.08	19	3.7877	9.5310	3.09	30
V4	20	0.40±0.05	0.23±0.04	13	3.7841	9.5169	3.20	70
Nb1	10	0.05±0.02	0.16±0.03	123	3.8078	9.6985	2.86	10
Nb2	20	0.72±0.04	0.013±0.002	117	3.8114	9.6141	2.80	15
Ta1	10	0.56±0.03	0.35±0.06	33	3.7936	9.5320	2.87	35
Ta2	20	0.35±0.07	0.02±0.01	67	3.7960	9.9141	2.87	10

The dopant precursor was vanadium (IV) triisopropoxide for V1 and V2, and vanadium (V) oxide for V3 and V4.

[a] The results are reported with 99.7% confidence interval

[b] The value of lattice parameters are calculated from XRD spectra

† band gap energy obtained from DRS measurements

** Crystallite sizes d are calculated from XRD peak widths

Table 3. Nominal and real element/Ti ratios and binding energies for XPS photolines of the doped TiO_2 samples.

Catalyst	Nominal value element/Ti (at.%/at.%) [a]	Real ratio element/Ti (at.%/at.%) [b]	Binding energy (eV) Ti2p		O1s		V2p	Ta4f		Nb3d	
V1	0.13	0.04	458.33	463.93	529.68	532.21	515.91	—		—	
V2	0.25	0.11	458.42	463.98	529.69	531.19	516.34	—		—	
V3	0.32	0.04	458.67	464.33	530.44	532.81	517.32	—		—	
V4	0.65	0.56	457.15	462.7	529.41	532.09	515.86	—		—	
Nb1	0.16	0.16	458.14	463.86	529.71	532.14	—	—		206.83	209.64
Nb2	0.42	0.32	458.41	464.18	529.54	531.97	—	—		206.98	209.88
Ta1	0.26	0.20	458.44	464.11	529.21	530.47	—	22.59	26.87	—	
Ta2	0.42	0.17	458.33	463.81	529.84	531.98	—	21.42	26.56	—	

[a] The nominal value is obtained based on the input concentration of element vs. titanium.

[b] The real element/Ti ratio was determined by XPS.